Some consequences of the closure of the momentum Bloch functions

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We present a proof of the closure property of the momentum Bloch functions directly from the Schrödinger equation. We derive from this property several new relations involving the crystal potential, energy-band values at a fixed point in the first Brillouin zone, and the momentum matrix elements. These relations determine the crystal potential from the energy-band values and the Bloch functions at $\mathbf{k}=0$, and permit application of the $\mathbf{k}\cdot\mathbf{p}$ method to the momentum Bloch functions.

I. INTRODUCTION

In this paper, we present a new proof for the closure property of the momentum Bloch functions. We derive from it certain new and useful relations involving the crystal potential, energy band values at a fixed point in the Brillouin zone, and the momentum matrix elements.

It is well known that the Bloch functions can be written in the form[1]

$$\psi_{n\mathbf{k}}(\mathbf{x})=\sum_{\mathbf{G}}\phi_n(\mathbf{k}-\mathbf{G})e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{x}}\ , \tag{1}$$

where $\mathbf{G}$'s are the reciprocal-lattice vectors, and ϕ_n's are the momentum Bloch functions. It is also well known that a set of Bloch functions $\{\psi_{n\mathbf{k}}\}$ is complete and can be chosen to be orthonormal:[2]

$$\sum_{n,\mathbf{k}}\psi^*_{n\mathbf{k}}(\mathbf{x})\psi_{n\mathbf{k}}(\mathbf{x}')=\delta(\mathbf{x}-\mathbf{x}')\ , \tag{2}$$

$$\int_{\text{crystal}}d\mathbf{x}\,\psi^*_{n\mathbf{k}}(\mathbf{x})\psi_{n'\mathbf{k}'}(\mathbf{x})=\delta_{nn'}\delta(\mathbf{k},\mathbf{k}')\ . \tag{3}$$

Here $\mathbf{k}$'s are restricted to the first Brillouin zone (BZ), n is the band index, and $\delta(\mathbf{k},\mathbf{k}')$ is such that

$$\delta(\mathbf{k},\mathbf{k}')=\begin{cases}\delta_{\mathbf{k},\mathbf{k}'} & \text{if } \mathbf{k}\text{'s are discrete}\ ,\\ (2\pi)^3V_{01}^{-1}\delta(\mathbf{k}-\mathbf{k}') & \text{if } \mathbf{k}\text{'s are continuous}\ .\end{cases} \tag{4}$$

(V_{01} = crystal volume). It is somewhat less well known that the momentum Bloch functions satisfy the closure and orthonormality relations given by

$$\sum_{n}\phi^*_n(\mathbf{k}-\mathbf{G})\phi_n(\mathbf{k}-\mathbf{G}')=\delta_{\mathbf{G}\mathbf{G}'}\ , \tag{5}$$

$$\sum_{\mathbf{G}}\phi^*_n(\mathbf{k}-\mathbf{G})\phi_{n'}(\mathbf{k}-\mathbf{G})=\delta_{nn'}\ . \tag{6}$$

The orthonormality of ϕ_n's, Eq. (6), readily follows from the orthonormality of $\psi_{n\mathbf{k}}$'s, Eq. (3). To prove the closure property (5), however, one has generally relied on the properties of the Wannier functions and the relationship between the Wannier functions and the Bloch functions.[3] The reason is that Eqs. (1) and (2) cannot be used directly to demonstrate (5). The difficulty arises from the sums in (1) and (2). Equation (2) involves a continuous sum over $\mathbf{k}$'s that belong to a finite BZ. The sum in (1) involves an infinite number of discrete $\mathbf{G}$'s.

In the literature, Eqs. (2) and (3) are treated as the most fundamental building blocks of the crystal band theory. We believe, however, that Eqs. (5) and (6) are more fundamental. Our belief is motivated precisely by the difficulty of passing from (2) to (5). The reverse route has no difficulties. If one assumes (5) and (6), then all of the properties of $\psi_{n\mathbf{k}}$'s are derived in a trivial fashion. It is therefore desirable to have a proof of (5) and (6) directly from the Schrödinger equation, without reference to the Wannier and Bloch functions. In Sec. II we present such a proof. We also give the closure and orthornormality relations of the momentum Bloch functions when the spin-orbit interaction is taken into account.

In the subsequent sections we discuss some interesting consequences of the closure of the momentum Bloch functions. In Sec. III we derive a set of equations relating the crystal potential to the momentum Bloch functions and the band energies. In Sec. IV we obtain a set of differential equations in the momentum space for the momentum Bloch functions. This set permits application of the $\mathbf{k}\cdot\mathbf{p}$ method[4] directly to the momentum Bloch functions.

II. A NEW PROOF

Neglecting the spin-orbit coupling for the moment, the one-electron Hamiltonian and the corresponding time-independent Schrödinger equation can be written as

$$H=\frac{\mathbf{p}^2}{2m}+V(\mathbf{x})=\frac{\mathbf{p}^2}{2m}+\sum_{\mathbf{G}}\mathscr{V}_{\mathbf{G}}e^{i\mathbf{G}\cdot\mathbf{x}}\ , \tag{7a}$$

and

$$\left[-\frac{\hbar^2}{2m}\nabla^2+\sum_{\mathbf{G}}\mathscr{V}_{\mathbf{G}}e^{i\mathbf{G}\cdot\mathbf{x}}\right]\psi=E\psi\ . \tag{7b}$$

To determine the eigenvalues and eigenfunctions of (7b), we first express $\psi(\mathbf{x})$ in terms of its Fourier transform $\phi(\mathbf{k})$:

$$\psi(\mathbf{x})=\sum_{\mathbf{k}}\phi(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{x}} . \tag{8}$$

Note that in this expression $\mathbf{k}$ is an arbitrary momentum. It is not restricted to the first Brillouin zone. It can be discrete or continuous. If the crystal is of finite size, for example a rectangular slab, then $\mathbf{k}$'s are discrete and the sum in (8) is over $k_1=2\pi n/L_1$, $k_2=2\pi m/L_2$, and $k_3=2\pi p/L_3$, where n, m, and p are integers and L_1, L_2, and L_3 are the dimensions of the slab. If this macroscopic volume is periodically extended to the entire space, then $\mathbf{k}$'s become continuous and the sum in (8) should be interpreted as $(2\pi)^{-3}V_{01}\int d\mathbf{k}$, where $V_{01}=L_1L_2L_3$. Furthermore, the basis functions $\exp(i\mathbf{k}\cdot\mathbf{x})$ are orthonormal and complete in either case:

$$\int_{\text{crystal}} d\mathbf{x}\, e^{i\mathbf{k}\cdot\mathbf{x}}e^{-i\mathbf{k}'\cdot\mathbf{x}}=\delta(\mathbf{k},\mathbf{k}') , \tag{9a}$$

$$\sum_{\mathbf{k}}e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')}=\delta(\mathbf{x}-\mathbf{x}') . \tag{9b}$$

From now on we assume that V_{01} is of unit size: $L_1L_2L_3=1$.

Using (8), (9a), and (9b), one can transform (7b) into an eigenvalue equation for ϕ:

$$\left[\frac{\hbar^2\mathbf{k}^2}{2m}-E\right]\phi(\mathbf{k})+\sum_{\mathbf{G}}\mathscr{V}_{\mathbf{G}}\phi(\mathbf{k}-\mathbf{G})=0 . \tag{10}$$

This equation couples ϕ at different values of its argument. It can be recast in the form of a linear system of equations:

$$\sum_{\mathbf{G}'}M_{\mathbf{G},\mathbf{G}'}\phi(\mathbf{k}-\mathbf{G}')=E\phi(\mathbf{k}-\mathbf{G}) , \tag{11a}$$

or, in matrix notation,

$$M\underset{\sim}{\Phi}=E\underset{\sim}{\Phi} , \tag{11b}$$

where the column vector $\underset{\sim}{\Phi}$ has components $\phi(\mathbf{k}-\mathbf{G})$, $\phi(\mathbf{k}-\mathbf{G}')$, $\phi(\mathbf{k}-\mathbf{G}'')$, etc., and the matrix M has elements

$$M_{\mathbf{G},\mathbf{G}'}=\frac{\hbar^2(\mathbf{k}-\mathbf{G}')^2}{2m}\delta_{\mathbf{G},\mathbf{G}'}+\mathscr{V}_{-\mathbf{G}+\mathbf{G}'} . \tag{11c}$$

The matrix M is Hermitian, since the crystal potential $V(\mathbf{x})$ is real and therefore $\mathscr{V}_{-\mathbf{G}}=\mathscr{V}_{\mathbf{G}}^*$. Because M is Hermitian, it has real eigenvalues $E_n(\mathbf{k})$ equal in number to the dimension of M (some of these eigenvalues may be degenerate). To each $E_n(\mathbf{k})$ there corresponds a column vector $\underset{\sim}{\Phi}^{(n)}$. One is free to normalize these eigenvectors, and we assume that they are orthonormal:

$$(\underset{\sim}{\Phi}^{(n)*})^T\underset{\sim}{\Phi}^{(n')}=\delta_{nn'} . \tag{12}$$

When this equation is written in component form, it yields

$$\sum_{\mathbf{G}}\phi_n^*(\mathbf{k}-\mathbf{G})\phi_{n'}(\mathbf{k}-\mathbf{G})=\delta_{nn'} . \tag{6}$$

The Hermiticity of the matrix M also means that the set of $\{\underset{\sim}{\Phi}^{(n)}\}$ is linearly independent and thus complete. This follows from the fact that the matrix U formed from $\underset{\sim}{\Phi}^{(n)}$, $U=(\underset{\sim}{\Phi}^{(1)},\underset{\sim}{\Phi}^{(2)},\ldots)$, is unitary and therefore $\det(U)\neq 0$. The unitarity of U, that is, $UU^{\dagger}=I$, means that

$$\sum_{n}\underset{\sim}{\Phi}^{(n)}(\underset{\sim}{\Phi}^{(n)*})^T=I , \tag{13}$$

or in component form:

$$\sum_{n}\phi_n^*(\mathbf{k}-\mathbf{G})\phi_n(\mathbf{k}-\mathbf{G}')=\delta_{\mathbf{G}\mathbf{G}'} . \tag{5}$$

So far $\mathbf{k}$ is an arbitrary vector parameter carried along (10)–(13). If $\mathbf{k}$ is not small enough to fall into the first Brillouin zone (1BZ), then there is a reciprocal-lattice vector $\mathbf{G}$ such that $\mathbf{k}=\mathbf{k}'+\mathbf{G}$ and $\mathbf{k}'\in 1\text{BZ}$. When the equations above are rewritten in terms of $\mathbf{k}'$, everything remains the same except for relabeling of the components of $\underset{\sim}{\Phi}^{(n)}$ and the elements of M. This relabeling has no effect on a given eigenvalue E_n. Therefore E_n is periodic in the reciprocal-lattice space: $E_n(\mathbf{k})=E_n(\mathbf{k}+\mathbf{G})$. For this basic result of the band theory, our line of reasoning provides a different method of proof than those usually encountered in textbooks. From now on, in order to fix the labeling, we assume that $\mathbf{k}$ is confined to the 1BZ.

As a side note we point out that it is the periodicity of the energy eigenvalues that justifies the writing of the Bloch functions in the form (1). To verify this statement, we rewrite (10) as

$$\frac{\hbar^2(\mathbf{k}-\mathbf{G})^2}{2m}\phi_n(\mathbf{k}-\mathbf{G})=E_n(\mathbf{k})\phi_n(\mathbf{k}-\mathbf{G})-\sum_{\mathbf{G}'}\mathscr{V}_{\mathbf{G}'}\phi_n(\mathbf{k}-\mathbf{G}-\mathbf{G}') , \tag{14}$$

making use of the periodicity of E_n. Next we operate on $\psi_{n\mathbf{k}}$ with H and use (14):

$$\begin{aligned}H\psi_{n\mathbf{k}}&=V\psi_{n\mathbf{k}}+\sum_{\mathbf{G}}\frac{\hbar^2(\mathbf{k}-\mathbf{G})^2}{2m}\phi_n(\mathbf{k}-\mathbf{G})e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{x}}\\&=V\psi_{n\mathbf{k}}+E_n(\mathbf{k})\psi_{n\mathbf{k}}-\sum_{\mathbf{G}'}\mathscr{V}_{\mathbf{G}'}e^{i\mathbf{G}'\cdot\mathbf{x}}\left[\sum_{\mathbf{G}}\phi_n(\mathbf{k}-\mathbf{G}-\mathbf{G}')e^{i(\mathbf{k}-\mathbf{G}-\mathbf{G}')\cdot\mathbf{x}}\right]\\&=E_n(\mathbf{k})\psi_{n\mathbf{k}} .\end{aligned} \tag{15}$$

Thus, the periodicity of E_n plays a crucial role in demonstrating that the superposition of ϕ_n's in (1) yields an eigenfunction of H.

When the spin-orbit interaction is taken into account, the Hamiltonian acquires the term

$$H_{\text{s.o.}}=\frac{\hbar^2}{4m^2c^2}\sum_{\mathbf{G}}e^{i\mathbf{G}\cdot\mathbf{x}}[\mathscr{V}_{\mathbf{G}}(\boldsymbol{\sigma}\times\mathbf{G})\cdot\nabla] . \tag{16}$$

The Bloch functions in the ordinary space, as well as in the momentum space, become two-component spinors.

The Fourier transform relation (8) is modified to

$$\psi_\mu(\mathbf{x})=\sum_{\mathbf{k}}\phi_\mu(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{x}}\ , \tag{17}$$

where $\mu=1,2$ refer to the spin-up and spin-down components. The Schrödinger equation corresponding to (10) becomes

$$\left[\frac{\hbar^2\mathbf{k}^2}{2m}-E\right]\phi_\mu(\mathbf{k})+\sum_{\mathbf{G},\mu'}\mathscr{V}_{\mu\mu'}(\mathbf{k},\mathbf{G})\phi_{\mu'}(\mathbf{k}-\mathbf{G})=0\ , \tag{18a}$$

where

$$\mathscr{V}_{\mu\mu'}(\mathbf{k},\mathbf{G})=\mathscr{V}_{\mathbf{G}}\left[\delta_{\mu\mu'}-\frac{i\hbar^2}{4m^2c^2}[\boldsymbol{\sigma}\cdot(\mathbf{k}\times\mathbf{G})]_{\mu\mu'}\right]\ , \tag{18b}$$

$$\boldsymbol{\sigma}=\hat{\mathbf{x}}\sigma_x+\hat{\mathbf{y}}\sigma_y+\hat{\mathbf{z}}\sigma_z\ , \tag{18c}$$

and $\sigma_{x,y,z}$ are the Pauli matrices. We again rewrite (18a) in the matrix form (11b) by defining the matrix

$$M_{\mathbf{G}\mu,\mathbf{G}'\mu'}=\frac{\hbar^2(\mathbf{k}-\mathbf{G})^2}{2m}\delta_{\mathbf{G}\mathbf{G}'}\delta_{\mu\mu'}+\mathscr{V}_{-\mathbf{G}+\mathbf{G}'}\left[\delta_{\mu\mu'}-\frac{i\hbar^2}{4m^2c^2}\{\boldsymbol{\sigma}\cdot[\mathbf{k}\times(-\mathbf{G}+\mathbf{G}')]\}_{\mu\mu'}\right]\ . \tag{19}$$

Because σ's are Hermitian, M is again Hermitian, and the previous argument for (12) and (13) still holds. The only new feature is that the number of eigenvalues and eigenvectors are doubled. For each previous single component $\phi_n(\mathbf{k}-\mathbf{G})$, $\underset{\sim}{\Phi}^{(n)}$ has now a two-component column vector. Furthermore each band designated by n is no longer purely spin up or spin down, but is a superposition of the spin-up and spin-down states. This mixing arises from the spin-orbit coupling. Writing (12) and (13) in component form for the spin-orbit case, we find

$$\sum_{\mathbf{G},\mu}\phi^*_{n\mu}(\mathbf{k}-\mathbf{G})\phi_{n'\mu}(\mathbf{k}-\mathbf{G})=\delta_{nn'} \tag{20a}$$

and

$$\sum_{n}\phi^*_{n\mu}(\mathbf{k}-\mathbf{G})\phi_{n\mu'}(\mathbf{k}-\mathbf{G}')=\delta_{\mu\mu'}\delta_{\mathbf{G}\mathbf{G}'}\ . \tag{20b}$$

One can readily show that

$$\psi_{n\mathbf{k}\mu}(\mathbf{x})=\sum_{\mathbf{G}}\phi_{n\mu}(\mathbf{k}-\mathbf{G})e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{x}} \tag{21}$$

is an eigenfunction of $H=p^2/2m+V+H_{\text{s.o.}}$ with eigenvalue $E_n(\mathbf{k})$, using the periodicity of $E_n(\mathbf{k})$ with respect to reciprocal-lattice vectors. The argument is exactly analogous to the one accompanying Eqs. (14) and (15).

III. CRYSTAL POTENTIAL AND MOMENTUM BLOCH FUNCTIONS

The closure property of the momentum Bloch functions yields several new and interesting relations concerning the crystal potential. To derive these relations we again ignore the spin-orbit interaction at first and set $\mathbf{G}=0$ in (14). Multiplying the resulting equation with $\phi_n(\mathbf{k}-\mathbf{G})$, summing over n, and using (5), we find

$$\mathscr{V}_{\mathbf{G}}=\sum_n E_n(\mathbf{k})\phi^*_n(\mathbf{k}-\mathbf{G})\phi_n(\mathbf{k})-\frac{\hbar^2\mathbf{k}^2}{2m}\delta_{\mathbf{G},0}\ . \tag{22a}$$

Clearly the $\mathbf{k}$ dependence of E_n's and ϕ_n's must be such that the right-hand side must be independent of $\mathbf{k}$, since the left-hand side is independent of $\mathbf{k}$. Setting $\mathbf{k}=0$, Eq. (22a) reduces to an even simpler form:

$$\mathscr{V}_{\mathbf{G}}=\sum_n E_n(0)\phi^*_n(-\mathbf{G})\phi_n(0)\ . \tag{22b}$$

In other words, crystal potential can be obtained from band energies and Bloch functions at $\mathbf{k}=0$.

One can use (22a) to write $V(\mathbf{x})$ in terms of $u_{n\mathbf{k}}(\mathbf{x})$:

$$V(\mathbf{x})=-\frac{\hbar^2\mathbf{k}^2}{2m}+\sum_n E_n(\mathbf{k})\phi_n(\mathbf{k})u^*_{n\mathbf{k}}(\mathbf{x})\ . \tag{23a}$$

Again, the $\mathbf{k}$ dependence must cancel out in the overall expression on the right-hand side. If we set $\mathbf{k}=0$, (23a) simplifies to

$$V(\mathbf{x})=\sum_n E_n(0)\phi_n(0)u^*_{n0}(\mathbf{x})\ . \tag{23b}$$

Equations (23a) and (23b) are consistent with the fact that the set of functions $\{u_{n\mathbf{k}}\,|\,\mathbf{k}=\text{fixed}\}$ is complete with respect to periodic functions.[5] Any periodic function such as V can be expanded in terms of the members of this set. Equations (19a) and (19b) give the coefficients of this expansion. Remarkably, the coefficients are just products of the energy eigenvalues and the momentum Bloch functions at a fixed $\mathbf{k}$.

We note that the energy eigenvalues appearing in Eqs. (22) and (23) are the actual energy values of the crystal relative to the vacuum, which is clear from the proof of the closure in the previous section. We also note that not all bands contribute to V. From (22b), we see that for a band to contribute to $\mathscr{V}_{\mathbf{G}}$ its Bloch function must be such that the periodic part of the Bloch function, $u_{n\mathbf{k}}=e^{-i\mathbf{k}\cdot\mathbf{x}}\psi_{n\mathbf{k}}$, has a nonzero average over the primitive cell. The last statement follows from the fact that ϕ_n and $u_{n\mathbf{k}}$ are related by

$$\phi_n(\mathbf{k}-\mathbf{G})=\frac{1}{\Omega}\int_\Omega d\mathbf{x}\,e^{i\mathbf{G}\cdot\mathbf{x}}u_{n\mathbf{k}}(\mathbf{x})\ , \tag{24}$$

where Ω is the volume of the primitive cell. Thus, $\phi_n(0)$ is nonzero only if $\int_\Omega d\mathbf{x}\,u_{n0}(\mathbf{x})\neq 0$.

Equations (23a) and (23b) impose self-consistency conditions on $\mathscr{V}_{\mathbf{G}}$, E_n, and ϕ_n, which can be useful for performing approximate calculations of the band structure. In such calculations one can start with some reasonable guesses for ϕ_n's and use the experimental values of E_n's at a fixed point in the 1BZ to obtain $\mathscr{V}_{\mathbf{G}}$'s. These $\mathscr{V}_{\mathbf{G}}$'s can then be used in the Schrödinger equation to obtain a new set of ϕ_n's, and the procedure can be repeated until the convergence of ϕ_n's is achieved. E_n versus $\mathbf{k}$ in the rest of the BZ can be determined directly via

$$E_n(\mathbf{k})=\sum_{\mathbf{G}}\frac{\hbar^2(\mathbf{k}-\mathbf{G})^2}{2m}\,|\,\phi_n(\mathbf{k}-\mathbf{G})\,|^2 + \sum_{\mathbf{G},\mathbf{G}'}\mathscr{V}_{\mathbf{G}'}\phi_n^*(\mathbf{k}-\mathbf{G})\phi_n(\mathbf{k}-\mathbf{G}-\mathbf{G}')\,, \tag{25}$$

which is obtained from (6) and (10).

When the spin-orbit interaction is taken into account, Eqs. (22a) and (22b) are slightly modified. The new relations can be derived from (14), appropriately modified for the spin-orbit interaction:

$$\frac{\hbar^2(\mathbf{k}-\mathbf{G})^2}{2m}\phi_{n\mu}(\mathbf{k}-\mathbf{G})+\sum_{\mathbf{G}',\mu'}\mathscr{V}_{\mu\mu'}(\mathbf{k},\mathbf{G})\phi_{n\mu'}(\mathbf{k}-\mathbf{G}-\mathbf{G}')=E_n(\mathbf{k})\phi_{n\mu}(\mathbf{k}-\mathbf{G})\,. \tag{26}$$

Setting $\mathbf{G}=0$, multiplying by $\phi^*_{n\mu''}(\mathbf{k}-\mathbf{G})$, summing over n, and relabeling, one finds

$$\sum_n E_n(\mathbf{k})\phi_{n\mu}(\mathbf{k})\phi^*_{n\mu'}(\mathbf{k}-\mathbf{G})=\frac{\hbar^2k^2}{2m}\delta_{\mathbf{G},0}\delta_{\mu\mu'}+\mathscr{V}_{\mathbf{G}}\left[\delta_{\mu\mu'}-\frac{i\hbar^2}{4m^2c^2}[\boldsymbol{\sigma}\cdot(\mathbf{k}\times\mathbf{G})]_{\mu\mu'}\right]\,. \tag{27}$$

One can now multiply both sides by $\delta_{\mu''\mu}+(i\hbar^2/4m^2c^2)[\boldsymbol{\sigma}\cdot(\mathbf{k}\times\mathbf{G})]_{\mu''\mu}$, and use the identity

$$(\boldsymbol{\sigma}\cdot\mathbf{A})^2=\mathbf{A}^2\,, \tag{28}$$

to find

$$\delta_{\mu\mu'}\mathscr{V}_{\mathbf{G}}\left[1+\frac{\hbar^4}{16m^4c^4}(\mathbf{k}\times\mathbf{G})^2\right]+\delta_{\mathbf{G},0}\delta_{\mu\mu'}\frac{\hbar^2k^2}{2m}=\sum_{n,\mu''}E_n(\mathbf{k})\left[\delta_{\mu\mu''}+\frac{i\hbar^2}{4m^2c^2}[\boldsymbol{\sigma}\cdot(\mathbf{k}\times\mathbf{G})]_{\mu\mu''}\right]\phi_{n\mu''}(\mathbf{k})\phi^*_{n\mu'}(\mathbf{k}-\mathbf{G})\,. \tag{29}$$

Setting $\mu=\mu'$, one obtains

$$\mathscr{V}_{\mathbf{G}}=-\delta_{\mathbf{G},0}\frac{\hbar^2\mathbf{k}^2}{2m}+\frac{\sum_{n,\mu''}E_n(\mathbf{k})\left[\delta_{\mu\mu''}+\frac{i\hbar^2}{4m^2c^2}[\boldsymbol{\sigma}\cdot(\mathbf{k}\times\mathbf{G})]_{\mu\mu''}\right]\phi_{n\mu''}(\mathbf{k})\phi^*_{n\mu}(\mathbf{k}-\mathbf{G})}{\left[1+\frac{\hbar^4}{16m^4c^4}(\mathbf{k}\times\mathbf{G})^2\right]}\,. \tag{30}$$

This equation must also hold for $\mathbf{k}=0$:

$$\mathscr{V}_{\mathbf{G}}=\sum_n E_n(0)\phi_{n\mu}(0)\phi^*_{n\mu}(-\mathbf{G})\,. \tag{31}$$

From (31), one also finds that

$$V(\mathbf{x})=\sum_n E_n(0)\phi_{n\mu}(0)u^*_{n0\mu}(\mathbf{x})\,. \tag{32}$$

IV. k·p METHOD WITH MOMENTUM BLOCH FUNCTIONS

The closure property (5) yields a set of differential equations in the $\mathbf{k}$ space, relating ϕ_n to the interband matrix elements of the position operator. This set permits direct applications of the $\mathbf{k}\cdot\mathbf{p}$ method[4] to the momentum Bloch functions.

The matrix elements of the position operator are given by[2]

$$\int_{\text{crystal}}d\mathbf{x}\,\psi^*_{n\mathbf{k}}\mathbf{x}\psi_{n'\mathbf{k}'}=-i\delta_{nn'}\frac{\partial}{\partial\mathbf{k}'}\delta(\mathbf{k},\mathbf{k}') +\delta(\mathbf{k},\mathbf{k}')\mathbf{X}_{nn'}(\mathbf{k})\,, \tag{33a}$$

where

$$\mathbf{X}_{nn'}(\mathbf{k})=\sum_{\mathbf{G}}\phi^*_n(\mathbf{k}-\mathbf{G})\left[i\frac{\partial}{\partial\mathbf{k}}\right]\phi_{n'}(\mathbf{k}-\mathbf{G})\,. \tag{33b}$$

The diagonal components of $\mathbf{X}$ are gauge dependent, and can be set $\mathbf{X}_{nn}=0$ for appropriate choices of $\mathbf{k}$-dependent phases for the Bloch functions.[2] The off-diagonal components of $\mathbf{X}$ are related to the interband matrix elements of the momentum operator and to the energy band separations:[2]

$$\mathbf{X}_{nn'}(\mathbf{k})=\frac{-i\hbar\mathbf{p}_{nn'}(\mathbf{k})}{m[E_n(\mathbf{k})-E_{n'}(\mathbf{k})]}\quad\text{for } n\neq n'\,. \tag{33c}$$

Thus the interband components of $\mathbf{X}$ are related to directly measurable quantities such as light-absorption coefficients and effective masses in different bands. These components also indicate the strength of coupling between different bands, for example, in the $\mathbf{k}\cdot\mathbf{p}$ perturbation theory.[4]

Equation (33b) can be converted into a linear system of differential equations for ϕ_n by multiplying it with $\phi_n(\mathbf{k}-\mathbf{G})$ on both sides, summing over n, and using (5). After relabeling the band indices, one has

$$\frac{\partial}{\partial\mathbf{k}}\phi_n(\mathbf{k}-\mathbf{G})=-i\sum_{n'}\phi_{n'}(\mathbf{k}-\mathbf{G})\mathbf{X}_{n'n}(\mathbf{k})\,. \tag{34}$$

Equation (34), together with boundary conditions at a fixed $\mathbf{k}$, determines ϕ_n's in terms of $\mathbf{X}_{nn'}$. Its form permits a method for approximate construction of ϕ_n's, and therefore $\psi_{n\mathbf{k}}$. In III-V and II-VI semiconductor compounds, there are small numbers of conduction and valence bands that are strongly coupled among them-

selves. Their coupling to other bands can usually be neglected, as in the $\mathbf{k}\cdot\mathbf{p}$ method.[4] With the same philosophy, if one restricts (34) just to these bands, then one has a finite and small number of differential equations which can be solved for ϕ_n. The corresponding approximate $\psi_{n\mathbf{k}}$'s are obtained from (1).

When the spin-orbit interaction is taken into account, $\mathbf{p}_{nn'}$ in Eq. (33) is replaced by the 2×2 matrix operator

$$\pi_{nn'}(\mathbf{k})=\mathbf{p}_{nn'}(\mathbf{k})+\frac{\hbar}{4mc^2}\int_{\text{crystal}} d\mathbf{x}\,\psi^{\dagger}_{n\mathbf{k}}(\sigma\times\nabla V)\psi_{n'\mathbf{k}'}\ . \tag{35}$$

$\mathbf{X}_{nn'}$ in (34) becomes a 2×2 matrix operator. As before, $\phi_n(\mathbf{k}-\mathbf{G})$ becomes a two-component spinor. The form of (34) remains unchanged otherwise.

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